

Origins of life, a Few Comments and an Update

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As a periodic note by an ISSOL president to researchers interested and likely involved in studies about the origin of life, I thought this would be a cheerful and easy to write update but, alas, as time goes by and research mounts it becomes more and more evident how uniquely difficult the search for origins is. Louis Lerman put it quite well recently¹: "Origins problems are the most conjectural and qualitative of scientific questions. It is hardly surprising then that the origin of life, like the origin of the universe, lacks uniquely defining quantitative assumptions and initial conditions. Individually, they are Fermi questions of a functional sort, requiring the use of a first-principle conceptual approach to a situation of fundamental quantitative ignorance". It is this ignorance that, albeit being the search actively ongoing, has by necessity widened its scope to involve so many disciplines that reading the relevant literature today has become a bewildering experience. So, for this sort of State of ISSOL commentary that I was asked to write, I will retreat to my lab-rat reminiscences (I am an old lady after all and there are many), comments on impressive recent papers and avoid observations on what will come next.

Reminiscences of course are in regard to my analyses of meteorites of over thirty years and I don't think I ever shared, if not with close friends, how the first detection of enantiomeric excesses (ee) in meteoritic amino acids² came to be. You may know or remember that the study of meteorites received its modern re-start with the fall of the Murchison meteorite in 1969³. It was the finding that this extraterrestrial rock contained organic compounds that originated the theme of "from stars to life" for origin(s) of life studies, i.e., brought home the idea the cosmic history of the biogenic elements was relevant in supplying the feedstock for that origin. Murchison was found chock-full of extraterrestrial organics, however, the particular search for their possible chiral asymmetry had proved to be controversial. Given the overwhelming homochirality of so many biomolecules and the ease with which they could have contaminated the meteorite, it is fair to say that everyone stayed away from the subject well into the '90s.

In the summer of 1996, however, it so happened that I was trying to clarify the distribution of 7-C amino acids in Murchison, I had synthesized most of them but the difficulty was to separate them chromatographically. Thinking of the various ways to do that I came up with the idea to utilize the same liquid chromatography column I had used for hydrocarbons, by what logic I can't remember, it had not been tried before and I only vaguely recall thinking of possible silica's OHs and buffer interactions. For some reason it worked, nothing to patent or boast about because it wasn't simple (each fraction collected required at least two hours of processing), but I was able to obtain, from standards and then from Murchison extracts, samples of individual long chain amino acids,

which when analyzed by GCMS showed a set of diastereomer enantiomers unknown in the biosphere *and* showing L-ee!

I don't think there ever was a more pedestrian "discovery" Why recall it then? Well, it is hard to tell how scientific research progresses and how to optimize it will vary with field of study, availability of tools, opportunities, etc., but it seems safe to point out that aimed curiosity for the unknown and its meticulous pursuit, the sweat of lab work included, more often than not will lead to significant findings and even the privilege of discovery.

In the category of success from extensive and meticulous experimentation (but far from pedestrian) is a recent finding I found most captivating. It was based on the extensive work by Eschenmoser and his group on the "chemical etiology of nucleic acid structure"⁴, in which they tested the base pairing properties of a large number of nucleic acids derived from various alternative sugar-phosphate backbones and tagged with canonical nucleobases. As R. Krishnamurthy reports in an Account of Chemical research⁵, while investigating the base-pairing properties of structural nucleic acid analogs, he and his coworkers "encountered a relationship between the pK_a of a series of nonstandard (and canonical) nucleobases and the pH of the aqueous medium. This relationship appeared to correspond with the propensity of these molecules to self-assemble via Watson-Crick-type base-pairing interactions and a simple pK_a-pH correlation enabled a general prediction of which types of heterocyclic recognition elements form hydrogen-bonded base pairs in aqueous media". This ability to rationalize why nature chose the canonical nucleobases in terms simply of hydrophobic and hydrophilic interactions and how organic compounds might have interacted with their aqueous environment is a very important step forward in the understanding of prebiotic chemical evolution and Krishnamurthy's paper is very worth reading.

Still regarding chemical evolution with a possible prebiotic bend, I was also impressed by a recent PNAS paper by Chackaborthy et al.⁶, describing how large amounts of ammonia can be formed by vacuum UV irradiation. Compared to other biogenic elements, such as H and C, N is a "funny" element because its two stable isotopes ¹⁴N and ¹⁵N are of partly primary/partly secondary stellar nucleosynthesis and this have brought some confusion in regard to their presolar distributions. Funny or not, however, the availability of reduced N is considered a must-have component for origin of life theories. The above group conducted experiments of N₂ photolysis at vacuum UV wavelengths in the presence of hydrogen, which produced ammonia with a wide range of δ¹⁵N enrichment values depending upon photodissociation wavelength. This experimental work shows, therefore, that during the early stages of the protoplanetary disc, such as during the T-Tauri stage, ammonia could have become present in our own solar system: habitability comes to mind.

Which leads me further in space, to cite last the large work done in the past few years in recognizing exoplanets. Kepler has discovered now thousands of candidate exoplanets (candidates, I am told by my astronomer consultant Steve Desch, because they must be distinguished from false positives like sunspots and follow-up observations or analyses are required to confirm these candidates as

true exoplanets). Recently on Jan 6, 2015, however, the 1000th Kepler candidate has been confirmed as an exoplanet (as part of a batch of 554 newly analyzed planets) and six of these newly confirmed exoplanets are in fact near-Earth-sized, and in their stars' habitable zones.

This is huge from an origin of life perspective, says Desch and I concur! Check it out:

<http://www.jpl.nasa.gov/news/news.php?release=2015-003>

See you all in Anchorage in 2017.

1. Learman L. 2010 The primordial bubble: water, symmetry breaking, and the origin of life. In: *Water and life: The unique properties of H₂O*. CR Press Ch.18 pp. 259-90.
2. Cronin JR & Pizzarello S. 1997 Enantiomeric excesses in meteoritic amino acids. *Science* 275, 951-55.
3. Kvenvolden K. et al. 1970 Evidence for extraterrestrial amino acids and hydrocarbons in the Murchison meteorite. *Nature* 228, 923-26.
4. Eschenmoser, A. 1999 Chemical Etiology of Nucleic Acid Structure. *Science* 284, 2118-24.
5. Krishnamurthy R. 2012 Role of pKa of Nucleobases in the Origins of Chemical Evolution. *Acc Chem Res* 45, 20035-44.
6. Chakraborty S. et al. 2014 Massive isotope effect in vacuum UV photodissociation of N₂ and applications for meteorite data. *Proc Natl Acad Sci USA* 111(41):14704-14709.